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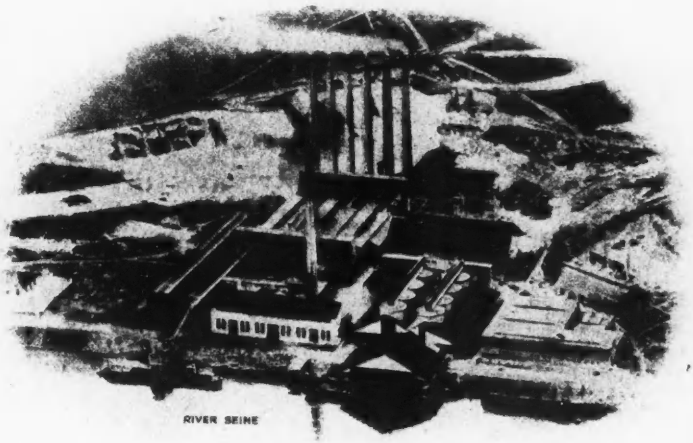

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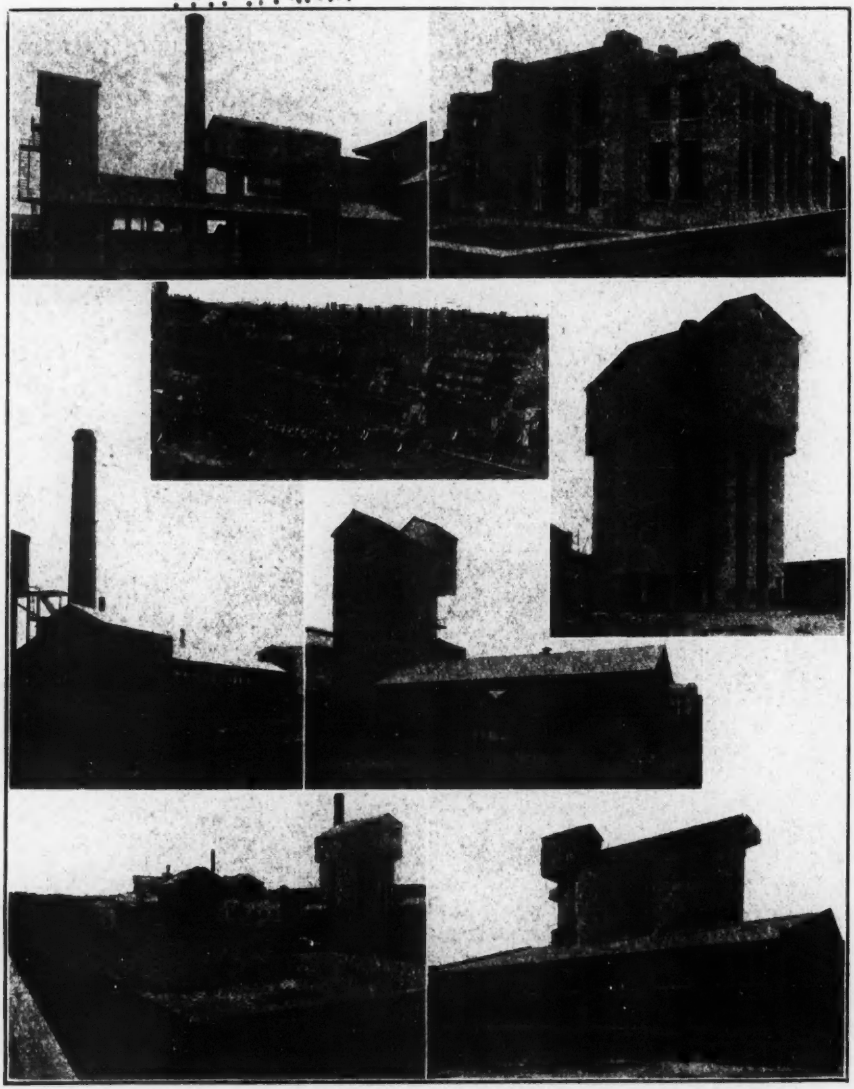

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Heat Transmission in Rotary Kilns.—VII.

By W. GILBERT, Wh.Sc., M.Inst.C.E.

(132) After calculating the rate of heat transmission in the 200-ft. rotary kiln with an exit-gas temperature of 950 deg. F., an improved method of calculation was devised for the drying zone, stages (1) to (5), in order to deal with kilns having exit-gas temperatures of 350 deg. F. or similar, such low temperatures being due to the provision of chains.

In Part III, para. (62) it was stated that the average inner surface temperature of the kiln lining in each of the five stages of the drying zone had been deduced in several kilns from measurements of the shell temperature and the corresponding thickness and conductivity of the firebrick lining. These figures are given in line (4) of Table XIII, Part V, and they are representative for kilns with exit-gas temperatures ranging from 750 deg. to 950 deg. F. As the lining temperature was approximately known in each stage it was not necessary to calculate the rate of heat transmission from the lining to the underside of the material charge, for reasons given in Part III, para. (66).

(133) In kilns having exit-gas temperatures ranging from 350 deg. to 500 deg. F. lower lining temperatures will obtain, especially in stages (1) and (2); hence it is now found preferable to standardise the rate of heat transfer from the lining to the underside of the material charge in each stage, and from these figures the average lining temperature and the average chain temperature can be deduced.

The symbol $H._{con}$ is used to denote the rate of heat transmission between the kiln lining and the underside of the material in the drying zone. It is expressed in B.T.U. per square foot per hour per deg. F. temperature difference. Since the heat is transferred mainly by conduction, emission and absorption factors are not used.

(134) As an example, the value of $H._{con}$ for stage (3) of the 200-ft. kiln may be obtained from the figures given in Part III, paras. (63 & 66). It is seen that 2103

B.T.U. per minute are transferred from the kiln lining to the underside of the material charge, also

Length of lower lining arc	5.15ft.
Average lining temperature..	660 deg. F.
Average material temperature	212 ,,
Average temperature difference	448 ,,

$$H._{con} = \frac{2103 \times 60}{5.15 \times 448} = 55.$$

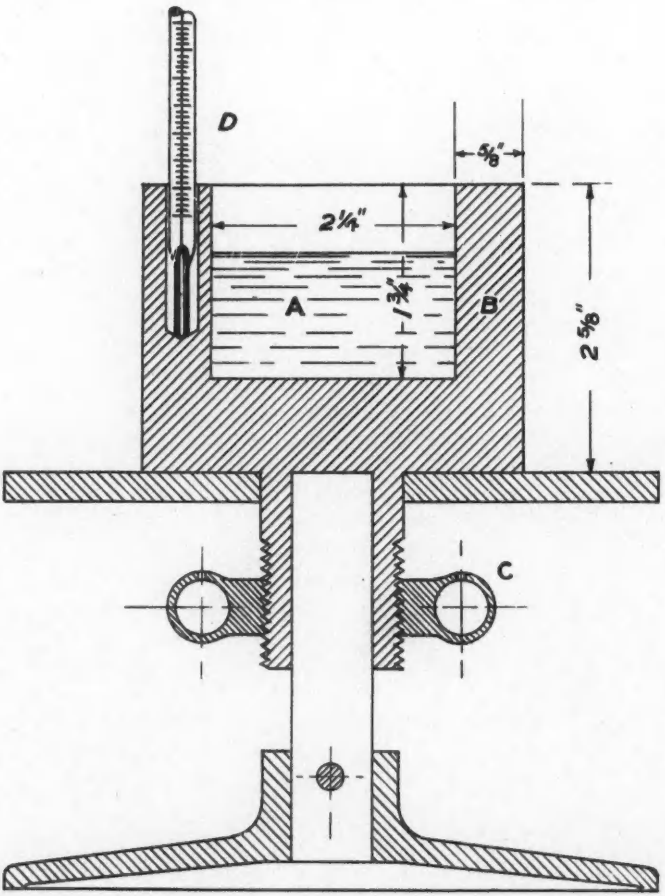


Fig. 26.

Proceeding in this manner the value of $H._{con}$ for each of the stages (1) to (5) of the 200-ft. kiln was found to be 186, 91, 55, 42, and 29 respectively. Values of $H._{con}$ are in all cases based on the average lining temperature (for circle), and not

on the average temperature of the lower lining arc. They are thus rather less than the true values.

(135) Some confirmation of these values for $H._{con}$ is considered desirable, and it may be obtained for stage (1) by small-scale experiments. The apparatus used for the purpose is shown in Fig. 26 ; it is essentially a small cylindrical furnace turned out of a copper block ; the interior (*A*) is $2\frac{1}{4}$ in. in diameter by $1\frac{3}{4}$ in. deep and the walls (*B*) are $\frac{5}{8}$in. thick. Heat is supplied by a gas ring (*C*) which is adjustable vertically. A thermometer (*D*) is placed in an air pocket which is drilled in the furnace wall. Owing to the high conductivity of copper and to the slow rate of heating the temperature of the inside wall of the thermometer pocket, and of the copper surfaces in contact with the slurry, will not differ by more than $\frac{1}{2}$ deg. F.

To make an experiment a charge of slurry is placed in the furnace and gently heated at a uniform rate from 60 deg. to 185 deg. F. or similar, the time occupied being 12 to 15 minutes. During heating the slurry is slowly stirred to maintain a uniform temperature throughout the mass and to prevent it from drying on to the heating surfaces. Its average temperature is obtained at frequent intervals by inserting a thermometer. At the end of the experiment curves are drawn to show the rate of heating of the furnace walls and the rate of heating of the slurry, and the apparent temperature difference at any instant can be obtained from them.

As the wall temperature rises the reading of the thermometer in the air pocket is less than the true temperature, and several experiments were made to determine what the lag of the thermometer would be for various rates of heating. In a typical experiment the average lag was 4.3 deg., and the average temperature difference from the curves 5.7 deg., giving a total of 10 deg. F.

During heating a small amount of moisture is evaporated ; in one experiment, for instance, the slurry moisture was 42 per cent. at the beginning, and 37.3 per cent. at the end.

(136) The heat supplied to raise the temperature of the slurry and to evaporate the moisture was calculated and compared with the area of the copper surfaces in contact with the slurry and with the true temperature difference. With slurry which originally contained 42 per cent. of moisture two typical experiments furnished values of $H._{con}$ of 156 and 161 respectively. A third experiment on slurry containing 50.6 per cent. of moisture gave $H._{con} = 177$.

For the sake of comparison a further series of experiments was made on the heating of water under similar conditions. The temperature was raised at a steady rate from 60 deg. F. to 185 deg. F. in about 15 minutes, the water being gently stirred. The proportion evaporated during heating was 3 per cent., or similar, which was measured and allowed for. These experiments gave values of $H._{con}$ of 366, 430, and 378 respectively.

(137) It is not practicable to use the apparatus shown in Fig. 26 to determine the value of $H._{con}$ for stages (2) to (5) where thick slurry or lumps of semi-dry

material are dealt with, since the average temperature difference between the furnace walls and the material surfaces in contact with them could not be readily measured.

The values of $H_{.con}$ as given in para. (134) were finally reconsidered, and somewhat amended. For stage (1) the result furnished by the small-scale experiments has been adopted. The figures for stages (2) and (3) remain as in para. (134), but in stages (4) and (5) they have been somewhat reduced. The values of $H_{.con}$ now used for calculation purposes are 150, 91, 55, 35, and 22.

Gas Radiation : Interference Due to Chains.

(138) Chains, where they occur, reduce the quantity of gas radiation which would otherwise fall on to the kiln lining or on to the material chord. The radiation to any square foot of the chain surface is also reduced by the shielding due

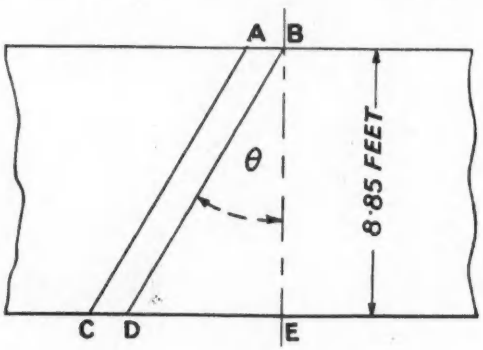


Fig. 27.

to adjacent lengths of chain. The extent to which shielding takes place is now investigated.

As mentioned in Part VI, para. (130), for calculation purposes the chains are replaced by a number of $\frac{3}{4}$-in. diameter balls which have the same surface area and which are uniformly distributed throughout the gas space of the kiln where the chains occur. Taking, for instance, stage (2) the kiln diameter is 8.85 ft. and the volume per foot run, after allowing for an 8 per cent. charge, is 56.6 cu. ft. The chain surface exposed to the gases is 26 sq. ft. per foot run of kiln, see para. (126), and the surface area of a $\frac{3}{4}$-in. diameter ball is 0.0123 sq. ft. Hence the number of balls per foot run of kiln is $\frac{26.0}{0.0123} = 2{,}118$, and the number per cubic foot of kiln volume is $\frac{2{,}118}{56.6} = 37.5$

(139) To lead up to the particular problem consideration is first given to Fig. 27, which represents a short length of stage (2) of the kiln under discussion.

A small area (AB) assumed plane is taken on the inside surface of the firebrick lining. Draw lines AC and BD each of which is inclined at an angle θ to the normal BE. All radiation from the area AB, which is inclined at θ to the normal and parallel to the plane of the paper, may be considered to pass along a tube $ABCD$, and it is desired in the first instance to find out how much of it would be intercepted by the $\frac{3}{4}$-in. balls distributed throughout the gas space. The absorption of the radiation from AB by the gas in the tube is neglected in this instance.

It will be seen that formulæ (2) and (3) in Part II are applicable to this problem. The area of a $\frac{3}{4}$-in. diameter ball in cross section is 0.00307 sq. ft. Using the same notation as in Part II, and taking the length AC or BD at 10 ft., we have

$$Na.D = 37.5 \times 0.00307 \times 10 = 1.151.$$

The corresponding value of F, the density factor, from Table V = 0.685. Hence only 0.315 of the radiation from AB which passes along the tube would reach the end CD.

(140) When, however, the radiation from the gas in the tube to the surface AB is considered, the loss due to shielding is considerably less. For calculation purposes the tube is divided into lengths of 1 ft., and the gas radiation due to each foot is considered separately.

In Fig. 27 the tube length is taken, for example, at 10 ft., but when the radiation which falls on to the surface AB from all directions inside the cylinder is suitably integrated, Professor Hottel states that the average length of the radiant beam is sensibly equal to the diameter of the cylinder. Hence the extent to which the gas radiation to the kiln lining is shielded by the $\frac{3}{4}$-in. balls is considered in this instance with reference to a tube of gas 8.85 ft. long which contains 37.5 balls per cubic foot.

The figures used for calculation purposes relate to stage (2) which contains chains throughout. From Table XIX in Part VI, the PD values for the gas radiation, when based on a kiln diameter of 8.85 ft., are 3.38 for H_2O and 1.45 for CO_2. The average gas temperature is 811 deg. F. The calculations in detail are given in Table XX.

TABLE XX.

(Cols. (2), (3), (6), and (7) are expressed in B.T.U. per sq. ft. per minute.)

Depth of gas layer (ft.) (1)	Total gas radiation. (2)	Gas radiation due to each foot of depth. (3)	Value of NaD. (4)	Value of F. (5)	Effective gas radiation due to each foot of depth. (6)	Total effective gas radiation. (7)
1	17.0	17.0	0.115	0.11	16.0	16.0
2	23.8	6.8	0.230	0.21	5.7	21.7
3	28.0	4.2	0.345	0.29	3.2	24.9
4	31.1	3.1	0.460	0.37	2.1	27.0
5	33.2	2.1	0.576	0.44	1.2	28.2
6	35.1	1.9	0.691	0.50	1.0	29.2
7	36.3	1.2	0.806	0.55	0.5	29.7
8	37.1	0.8	0.921	0.60	0.3	30.0
8.85	37.6	0.5	1.019	0.64	0.2	30.2

(141) Referring to Table XX, col. (1) shows the depth of gas in the equivalent tube as measured from the kiln lining. Col. (2) gives the radiation due to the gas depth in col. (1); the figures are obtained by putting $D = 1, 2, 3$, etc., in the PD values before using the tables of gas radiation. Col. (3), which is obtained from col. (2), shows the gas radiation due to each foot of depth. Col. (4) gives values of $Na.D$, the value of D in each line being taken from col. (1). Col. (5) shows the corresponding values of the density factor F. It will be seen that the values of F unlike the gas radiation, are nearly proportional to the depths in col. (1). Col. (6) is obtained from cols. (3) and (5). Taking for instance line (1), the gas radiation is 17 and the average shielding effect of the balls is assumed to be that due to half the depth, or 6 in. The value of F is sensibly $\frac{0.11}{2} = 0.055$, and the gas radiation which reaches the kiln lining is $17 \times (1 - 0.055) = 16.0$ as shown in col. (6). In line (2) the depth for shielding is 1.5 ft., hence $F = 0.16$ and the effective gas radiation due to the second foot of depth is $6.8 \times (1 - 0.16) = 5.7$.

(142) It will be seen from the last line of Table XX that the effect of the chains is to reduce the gas radiation to the lining from 37.6 to 30.2 B.T.U. per square foot per minute. Hence the shielding factor is

$$\frac{30.2}{37.6} = 0.80 \text{ nearly.}$$

Relatively large PD values are obtained in the wet end of a rotary kiln, and Table XX brings out the fact that an increase of kiln diameter beyond 5 or 6 ft. adds little to the gas radiation per square foot of lining area. When chains are used, however, a relatively large diameter is of advantage.

(143) SHIELDING FACTOR FOR CHAINS.—The gas radiation to the chains is obtained, per square foot of area, by using $0.55\ PD$, see Part VI, para. (130).

Now $0.55 \times 8.85 = 4.86$ ft. The unobstructed radiation due to 4.86 ft. is, from col. (2) of Table XX, about 32.9. The obstructed radiation from col. (7) is approximately 28.0. Hence the shielding factor is

$$\frac{28.0}{32.9} = 0.85$$

The values of the shielding factors as found, although based on the gas temperature and on the PD values of stage (2), are considered to be fairly representative, and are used for each stage of the kiln under discussion in which chains occur.

Stage Lengths in Drying Zone.

(144) The figures which enable the stage lengths in the drying zone to be calculated are given in Table XXI. The heat to be transmitted in each stage is obtained from Table XVIII in Part VI, but the superheat [see (116a)] is not included since it is performed by a mixing of the gases.

In stage (1) the heat required is 1.84 per cent. The first 16 ft. of the kiln (see Fig. 19) is without chains, and this forms stage (1A). It is found by calculation that stage (1A) can transmit 0.15 per cent., leaving 1.69 per cent. to be transmitted by stage (1B). Stage (2), in which one-fourth of the moisture is evaporated,

is provided with chains throughout. Beyond stage (2) there remains a short length of 1.9 ft. of kiln which contains chains, and this forms stage (3A). Stage (3B) is completed when one-half of the moisture is evaporated.

TABLE XXI.—HEAT TRANSMISSION IN DRYING ZONE.

		Raising Slurry Temperature.		Evaporation of Slurry Moisture.				
		(1A)	(1B)	(2)	(3A)	(3B)	(4)	(5)
1	Heat transmitted ... ... per cent. on clinker	0.15	(Chains) 1.69	(Chains) 2.24	(Chains) 0.12	2.24	2.36	2.35
2	Average gas temperature ... ... deg. Fah	507	594	811	957	1,131	1,516	1,993
3	Average lining temperature (circle) ... ,,	96	168	281	330	480	856	1,336
4	Average chain temperature ... ... ,,	—	214	367	452	—	—	—
5	Average material temperature ... ... ,,	66	142	212	212	212	212	212
6	Value of H(con.)	150	150	91	73	55	35	22
7	Shell radiation factor	0.081	0.032	0.032	0.032	0.081	0.081	0.081
8	Gas radiation to upper lining arc } All heat quantities in lines (8) to (14) are in B.T.U. per foot run of kiln per minute.	231	226	444	645	1,170	2,104	2,875
9	Gas convection to ,, ,, ,,	289	307	372	436	452	441	415
10	Gas radiation to material chord	66	73	133	193	334	682	1,111
11	Gas convection to ,, ,,	93	94	123	154	176	248	339
12	Gas radiation to chains... ...	—	235	465	657	—	—	—
13	Gas convection to ,, ...	—	1,630	2,000	2,346	—	—	—
14	TOTAL HEAT TRANSMITTED ...	679	2,565	3,537	4,431	2,132	3,475	4,740
15	Length in kiln required for stage ... ... ft.	16.0	48.0	46.1	1.9	78.4	49.5	36.2
16	Added length of stages ... ... ,,	16.0	64.0	110.1	112.0	190.4	239.9	276.1
17	Gas radiation ... ... per cent. of total	43.7	20.8	29.5	33.8	70.5	79.6	84.2

The average gas temperatures given in line (2) of Table XXI are based on the figures given in Table XVIII, Part VI, but since stages (1) and (3) are now subdivided the average gas temperature in each portion is deduced as the calculation proceeds. Lines (3) and (4) are calculated as explained later, and lines (5), (6) and (7) have already been dealt with.

Table XXI is further explained by the calculation in detail of the heat transmission in stage (2). The average lining temperature (for circle) and the average chain temperature are provisionally assumed and subsequently shown to be consistent.

Heat Transmission in Stage (2).

(145) Taking first the heat transmitted from the gas to the kiln lining, and to the material, the gas radiation at 811 deg. F., 281 deg. F., and 212 deg. F. is obtained from Tables II, III, and IV in Part II. The *PD* values are given in lines (13) and (14) of Table XIX in Part VI. The result is

Gas radiation at 811 deg. F. = 30.4 + 8.1 − 0.9 = 37.6
Do. at 281 ,, = 3.7 + 1.1 − 0 = 4.8
Do. at 212 ,, = 2.4 + 0.6 − 0 = 3.0

Table XIX also gives the convection constants, and the lengths of the upper and lower lining arcs and of the material chord.

The emission and absorption factors for the lining and for the material chord in the drying zone are 0.80 as before—see Table XIII.

The lining storage factor in the drying zone has been calculated by the Fourier Series for stages (4) and (5) and found to be 0.89 in each case. Since the temperature fluctuation in the lining is therefore small it is neglected for the sake

of simplicity throughout the drying zone, and the calculations in lines (8) and (9) are based on the average lining temperature (for circle).

In stages (1) and (2) a coating of slurry on the lining would probably reduce the fluctuation of the surface temperature as calculated.

(146) Referring again to Table XXI, the detail of lines (8) to (11) can now be given.

Line

(8) Gas radiation to upper lining arc
$(37.6 - 4.8) \times 0.8 \times 0.8 \times 21.18$ 444

(9) Gas convection to upper lining arc
$(811 - 281) \times \frac{1.99}{60} \times 21.18$ 372

(10) Gas radiation to material chord
$(37.6 - 3.0) \times 0.8 \times 0.8 \times 6.0$ 133

(11) Gas convection to material chord
$(811 - 212) \times \frac{2.06}{60} \times 6.0$ 123

In lines (8) and (10) the second factor 0.8 represents the shielding due to the chains, see para. (142).

Heat Transmitted to Chains in Stage (2).

(147) In Part VI, para. (130), it was shown that when estimating the heat transmitted by gas radiation to the chains it was necessary to use 0.55 D instead of D in the PD values; hence we have,

PD value for $H_2O = 0.55 \times 3.38 = 1.86$
PD value for $CO_2 = 0.55 \times 1.45 = 0.80$

and from the Tables

Gas radiation at 811 deg. F. $= 25.6 + 7.5 - 0.6 = 32.5$
Gas radiation at 367 ,, $= 4.8 + 1.4 - 0 = 6.2$

The detail of lines (12) and (13) of Table XXI is then

Line

(12) Gas radiation to chains
$(32.5 - 6.2) \times 0.8 \times 0.85 \times 26.0 =$ 465

(13) Gas convection to chains
$(811 - 367) \times \frac{10.4}{60} \times 26.0 = 2{,}000$

In line (12) the factor 0.85 represents the shielding due to adjacent chains [see para. (143)], and 26 is the chain area in square feet which is exposed to the hot gases [see para. (126)]. In line (13) the mean temperature of the gas and chains is $\frac{1}{2}(811 + 367) = 589$. From Table XIX, line (10), the gas velocity is 23.3 ft. per second, hence from Fig. 22 the value of H_c is 10.4 B.T.U. per sq. ft. per hour per deg. F. Since the calculations are based on heat transmission per minute the divisor 60 is introduced.

Verification of Lining Temperature.

(148) From Table XXI, lines (7) and (14), the shell radiation loss in stage (2) is $0.032 \times 3{,}537 = 113$ B.T.U. per foot run of kiln per minute. From lines (8) and (9) the lining receives 816 B.T.U. per minute, hence it transfers to the underside of the material $\frac{816 - 113}{6.62} = 106$ B.T.U. per square foot per minute.

Since the value of $H_{.con}$ for stage (2) is 91 [see para. (137)] it follows that the

average temperature difference T_d between the lower lining arc and the underside of the material is given by

$$T_d \times 91 = 106 \times 60, \text{ hence } T_d = 70 \text{ deg. F.}$$

Hence the average lining temperature is 212 deg. + 70 deg. = 282 deg. F. This compares with 281 deg. F. assumed in line (3) of Table XXI.

Verification of Average Chain Temperature.

(149) From lines (12) and (13) the heat supply to the chains is 2,465 B.T.U. per minute, the surface area buried in the slurry at any instant is 10.5 sq. ft. [see (126)], and $H_{.con}$ for stage (2) is 91. Hence the average temperature difference between the chains and the slurry is given by

$$T_d \times 91 \times 10.5 = 2{,}465 \times 60.$$

Hence $T_d = 155$ deg. F. and the average chain temperature is 212 + 155 = 367 deg. F. as shown in line (4) of Table XXI.

It will be seen that the average temperature of the chains at any cross section depends on the rate at which they can give up their heat to the slurry, hence the rapidly falling values of $H_{.con}$ in stages (3) and (4) due to the small lumps of slurry becoming dry on the surface, will limit the distance to which the chains can be carried down the kiln.

(150) LENGTH REQUIRED FOR STAGE (2).—The clinker output [see para. (111a)] is 578.5 lb. per minute, and a heat transmission of 1 lb. of standard coal per 100 lb. of clinker is

$$5.785 \times 12{,}600 = 72{,}890 \text{ B.T.U. per minute.}$$

In stage (2) the heat to be transmitted is [from line (1) of Table XXI] 2.24 per cent.; also, from line (14), the heat transmitted per foot run of kiln per minute is 3,537 B.T.U. Hence the length required for stage (2) is

$$\frac{2.24 \times 72{,}890}{3{,}537} = 46.1 \text{ ft., as shown in line (15).}$$

It will be seen from line (16) that the dry raw material line is estimated to occur at a distance of 276.1 ft., from the feed end of the kiln.

How Far Down the Kiln May the Chains Go?

(151) From Table XXI the average chain temperature in the short stage (3A) is 452 deg. F. Since this is not excessive the chains are provisionally assumed to extend to the end of stage (3B), that is, to the point where the slurry is half dry. The heat transmission calculations for stage (3), if entirely filled with chains, are as follows, the line numbers referring to Table XXI:

Line		B.T.U.
(8) to (11)	Heat transfer from gas to upper lining arc and to material chord	1,865
(12)	Gas radiation to chains	932
(13)	Gas convection to chains	2,580
	Total	5,377

The average chain temperature is found to be 577 deg. F., and the stage length becomes

$$\frac{2.36 \times 72{,}890}{5{,}377} = 32.0 \text{ ft.}$$

It will be seen from line (15) of Table XXI that the kiln is now shortened by 1.9 + 78.4 − 32.0 = 48.3 ft., if the output and exit gas temperature remain as before.

(152) To obtain the maximum temperature reached by the chain, an equivalent ring 1 ft. wide is taken at the lower end of stage (3). Calculations similar to those given in para. (151) show that the chains receive 4,028 B.T.U. per minute, and the average chain temperature at the point considered is 722 deg. F.

The chains store the heat which they receive from the kiln gases and give it out later to the slurry, hence their temperature must pass through a maximum and a minimum during each revolution of the kiln. Since the chains weigh 14.4 tons and extend for a length of 96 ft., their weight per foot run of kiln is 366 lb.; hence at the end of stage (3) each pound of chain receives and gives up

$$\frac{4{,}028}{366} = 11.0 \text{ B.T.U. per minute, or per revolution.}$$

Taking the specific heat of iron to be 0.115, the fluctuation of the chain temperature is $\frac{11.0}{0.115} = 96$ deg. F. The maximum chain temperature is thus 722 + 48 = 770 deg. F. It does not seem advisable to carry the chains beyond the end of stage (3), where the slurry is half dry, partly because the specific heat of iron is low and the chains may reach a high temperature during the starting up of the kiln when the charge is dry, and the value of $H_{.con}$ small. The writer would prefer to proportion the kiln so that the exit-gas temperature was reduced to 375 deg. F. without carrying the chains beyond the middle of stage (3).

Length of Kiln if Without Chains.

(153) To throw further light on the subject, the lengths of stages (1), (2) and (3) have been recalculated on the assumption that the chains are omitted. The result is shown in Table XXII.

TABLE XXII.—KILN WITHOUT CHAINS.

Stage No. (1)	Heat transmitted. Per cent. on clinker. (2)	Average gas temperature. Deg. F. (3)	Average lining temperature. Deg. F. (4)	Heat transmitted per foot run of kiln B.T.U. per minute. (5)	Length required for stage. Ft. (6)
1	1.84	587	171	748	179.0
2	2.24	811	305	1198	136.0
3	2.36	1122	475	2080	82.6
4	—	—	as before	—	49.5
5	—	—	do. do.	—	36.2
				Total	483.3

From line (16) of Table XXI the length of the drying zone at present is 276.1 ft.; hence, if the chains are omitted the kiln would have to be lengthened by 483.3 − 276.1, or 207.2 ft., in order to obtain the same result.

The calculations relating to stages (6) and (7) and to the combustion zone of the 400-ft. kiln will be completed in the next article.

(To be continued.)

The Chemical Constitution of Portland Cement Clinker.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

NOTWITHSTANDING the work of scores of investigators, the constitution of Portland cement clinker is a subject which cannot be considered to be completely understood. Portland cement may be defined as the material obtained by finely pulverising clinker produced by calcining to incipient fusion an intimate and properly proportioned mix of argillaceous and calcareous materials, with no additions subsequent to calcination except water and calcined or uncalcined gypsum. The main substances of clinker formation are therefore calcium oxide, silica, alumina and iron oxide, and the problem of the constitution of Portland cement depends very largely on the elucidation of the possible interactions of these four components.

Early Work.

There was no real speculation as to the constitution of Portland cement clinker until Fuchs[1] in 1832 maintained that the only object of calcination was the dissociation of the clay and limestone whereby the silica of the clay was brought into such a condition that it could combine with the lime when the product was mixed with water. Pettenkoffer[2] and Feichtinger[3] supported this theory. Rivot and Chatonney[4] in 1836 suggested for the first time that the hydraulic property of cement might be due to the formation of a silicate of lime, an aluminate of lime and a silico-aluminate forming hydrated salts under the action of water. Heldt[5] in 1853 claimed that an active silicate and an inert aluminate were formed. Fremy[6] claimed to have prepared a variety of calcium silicates, aluminates, and double silicates of lime and alumina, and reported the aluminates to be hydraulically active and the silicates inert. He therefore believed that Portland cement clinker contained calcined aluminates and silicates, a calcium silico-aluminate, and free lime, and that the aluminates became hydrated and the free hydrated lime reacted with the silicates and silico-aluminate.

Petrographic Investigations.

Le Chatelier[7] was the first to examine clinker by the petrographic method. He found that Portland cement clinker contained the following constituents: (1) Double refracting colourless crystals, the most abundant constituent. (2) Slightly yellow brown crystals. Their shape and dimensions resemble (1) but they are distinguished by their colour and by very fine striæ and absence of transparency. This constituent is always present. (3) A dark yellow-orange to greenish-brown mass, with strong birefraction, occurring between the crystals of (1). This constituent is always present. (4) Very small colourless crystals, with strong double refraction. This constituent is only present in underburned cements. (5) Certain undistinguished constituents.

Törnebohm[8] carried out a petrographic examination of clinker in 1897 and confirmed the work of Le Chatelier in all its essentials. He also attempted the

separation of the constituents of clinker by means of liquids of high specific gravity. He identified four crystalline constituents and an isotropic colourless glass as follows: Alite—the most abundant constituent; Belite; Celite—between the crystals of Alite; Felite—found in small and variable quantity and often absent, isotropic colourless glass with a refractive index as high or higher than that of Alite. Alite, Belite, Celite and Felite are Nos. 1, 2, 3 and 4 in Le Chatelier's classification. It thus became evident that Portland cement clinker was a system of several minerals.

Stern[9] studied the micro-structure of clinker sections. Polished sections were observed with reflected light and thin sections by transmitted light. He found that in all normal clinkers there are two chief constituents. One was shown to consist of hard crystalline aggregates identical with the Alite of Törnebohm; the other consisted of softer particles surrounding the Alite.

Richardson[10] reported that the two prominent constituents of cement clinker were (1) a colourless mass of more or less crystalline form (Alite), and (2) a yellowish material surrounding (1) and devoid of all crystalline outlines (Celite). These substances were always present, but the form, size of crystal, and distribution were very variable due to several causes, such as (1) chemical composition, homogeneity, and fineness of the raw mix; (2) time and temperature of burning; (3) rate of cooling.

The petrographic examination of clinker was revised and extended in 1912 by von Glasenapp[11] who considered that clinker minerals are probably not simple chemical compounds but a continuous range of mixtures of various constituents.

Hattori[12] carried out a microscopical examination of thin sections of clinker and examined the surfaces after etching with water, dilute HCl, and dilute HF. The etched surfaces showed two predominating constituents, namely, Alite crystals in a ground mass identical with the Celite of other workers. The ground mass consisted of two different substances, one white and the other grey when examined by reflected light. The amount of Alite increased as the proportion of calcium oxide in the clinker increased.

By the petrographic examination of a great number of clinkers of widely different origin and composition, Guttmann and Gille[13] found nine different clinker constituents. (1) Alite was the most abundant constituent. (2) Belite was distinguished from Alite by its colour and its powerful double refraction; it is optically positive; it forms modifications which crystallise partly in the rhombic and partly in the monoclinic system. (3) Celite, which generally crystallises in needles or plates of high refractive index; it comprises all the dark, almost opaque portions of the clinker; it perhaps contains several substances of very similar composition; its composition is indefinite. (4) Felite, a substance practically never found except in "dusted" clinkers; it shows pronounced striations. (5) Glass, which is the amorphous ground mass, and contains a considerable proportion of alumina; in cements rich in iron this glass may be coloured brown by iron oxide, so that it may readily be confused with the clinker minerals of the Celite class. (6) β-Dicalcium silicate, a tetragonal modification

only occasionally observed in thin sections of clinker. (7) Calcium oxide, optically isotropic ; typical in insufficiently burned clinker or in over-limed clinker. (8) Calcium aluminates, which occur in clinkers relatively high in alumina. (9) Epezite, a constituent first found by Guttmann and Gille, and which previously had generally been confused with Alite ; it only occurs occasionally and is feebly refracting but strongly double refracting and mostly appears in spherolithic form.

Generally only a few of these constituents are found in any individual clinker but Guttmann and Gille's object was to cover all possibilities. The optical properties of these constituents are tabulated in Table I.

TABLE I.

Name.	Colour.	Refractive Index.			Double Refraction.	Crystal System.
		α	β	γ		
Alite	Colourless.	1.715	—	1.722	Feeble. Negative.	Monoclinic. Rhombic.
Belite	Brownish.	1.715	—	1.735	Strong. Positive.	Monoclinic. Rhombic.
Celite	Dark brown.	—	—	—	—	—
Felite	Colourless.	1.640	1.646	1.655	Strong. Negative.	Monoclinic.
Glass	—	—	—	—	—	—
β-dicalcium silicate.	Colourless.	—	1.715 (circa).	—	Positive.	Tetragonal.
Calcium oxide .	Colourless.	—	1.838	—	—	Regular.
Calcium aluminates :						
$3CaO.Al_2O_3$.	—	—	1.710	—	—	Isometric.
$5CaO.3Al_2O_3$	—	—	1.608	—	—	,,
Epezite	Colourless.	1.550	—	1.560	Strong. Positive. (Doubtful.)	Doubtful.

Relation of Crystalline Forms to Chemical Composition.

This problem has not yet been satisfactorily solved. There is a consensus of opinion as to the nature of the major constituent, but the exact forms in which the alumina and iron oxide exist are not definitely known.

LE CHATELIER.—Le Chatelier[7] propounded the theory that Portland cement was composed of two essential compounds, namely, tricalcium silicate, $3CaO.SiO_2$, and tricalcium aluminate, $3CaO.Al_2O_3$, and that the hydraulic properties of the cement are largely due to the tricalcium silicate. He considered that dicalcium silicate, $2CaO.SiO_2$, is not effective in this way. In support of this theory he analysed the " grappiers " or nodules remaining from the hard burning of certain siliceous limestones. The ground grappiers were found to give a good quality cement and their analysis showed them to consist largely of calcium oxide and silica in the proportion corresponding essentially to the formula $3CaO.SiO_2$. All Le Chatelier's efforts to synthesise tricalcium silicate failed. On heating together calcium oxide and silica in the proper proportions only a mixture of calcium silicates and free calcium oxide was formed. Attempts to produce tricalcium silicate by fusion methods were unsuccessful.

When he used calcium chloride as a flux Le Chatelier claimed to have obtained a crystalline chlorosilicate $2CaO.SiO_2.CaCl_2$. By passing water vapour at 450 deg. C. over the chlorosilicate he obtained a product which he thought was tricalcium silicate, the reaction being $2CaO.SiO_2.CaCl_2+H_2O=2HCl+3CaO.SiO_2$. Unfortunately the reaction was incomplete and the product could not be studied microscopically since it appeared amorphous. It seemed, however, to possess properties of setting and hardening; pats showed no swelling or cracking, indicating that free calcium oxide was absent. Le Chatelier concluded that the absence of free lime, together with the setting and hardening properties not possessed by the lower silicates, indicated a compound tricalcium silicate, $3CaO.SiO_2$, in cement and not a simple mixture whose properties would be the sum of those of the individual compounds.

The orthosilicate $2CaO.SiO_2$ was of special interest to Le Chatelier because it possessed the property of spontaneous disintegration, or dusting. He explained this as due to the presence of twin crystals, the unequal contraction of the opposite faces of which during the cooling process he held to be responsible for the disintegration observed. He claimed to have synthesised tricalcium aluminate, $3CaO.Al_2O_3$, and reported that more basic aluminates did not exist. He stated that mixtures of calcium oxide and ferric oxide on burning gave non-hydraulic products.

On heating mixtures of calcium oxide, alumina, and ferric oxide he reported the formation of two double compounds: (*a*) $3CaO.2(Al.Fe)_2O_3$ (deep brown colour), and (*b*) $3Ca_2O.Al_2O_3.Fe_2O_3$ (red needles). The formation of these bodies considerably augments the fusibility of cement clinker.

Le Chatelier, on reviewing his work, drew the following conclusions: (1) A Portland cement clinker of very high lime content consists essentially of tricalcium silicate and tricalcium aluminate, the former being the predominating and the main hydraulic constituent. (2) As the percentage of lime falls, silico-aluminates of the type $3CaO.Al_2O_3.2SiO_2$ eventually appear. In these compounds the ferric oxide may wholly or partially replace alumina. (3) As the percentage of lime falls still further, dicalcium silicate, $2CaO.SiO_2$, appears. (4) Calcium alumino-ferrites of the type $3CaO.2(Al.Fe)_2O_3$ are present. (5) The absence of free lime in well-burned clinker is very certain. Petrographic examination indicated that Alite is tricalcium silicate. The iron is contained mainly in the Celite. He did not identify the alumina in any of the petrographic constituents.

TÖRNEBOHM.—Törnebohm[8] attempted the separation of Alite from clinker by flotation methods with methylene iodide. The separation was not complete, as some Celite always remains with the Alite. He analysed the separated product and by assuming (*a*) 10 per cent. Celite still present by petrographic examination and (*b*) MgO and alkalis behave as CaO, he deduced the formula

$$9(3CaO.SiO_2) + 9CaO.2Al_2O_3$$

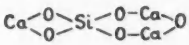
for Alite. Like Le Chatelier he failed to identify the alumina among the clinker constituents. He found that formulæ for constituents other than

Alite were very difficult to express and could not be definitely established chemically.

Törnebohm considered that Celite contained CaO and Fe_2O_3, some SiO_2, and probably some Al_2O_3. He thought it to be a double silicate of alumina, iron and calcium of no definite composition. It was a mother liquor separating after the other phases, and the composition varied with the conditions governing clinker formation. Felite, found in small quantity only in underburned cements, he considered to be probabiy a calcium aluminate. The isotropic colourless glass he reported as a double silicate of lime and alumina.

In the period from 1895 to 1900 several investigators put forward the view that free calcium oxide is present in rather large quantities in Portland cement clinker. Many methods of estimating free calcium oxide were tried, but these were of little value because (1) methods employing aqueous solutions are obviously inadmissible, and (2) the other methods used at that time are known to-day to be worthless. Rohland[14] stated that quantitative proof of the existence or non-existence of free CaO or $Ca(OH)_2$ was exceedingly difficult by purely chemical means.

Meyer[15] agreed with Le Chatelier on the essential points of clinker constitution. He concluded by microscopic examination and by estimating free lime in lightly burnt clinkers that it is impossible for free lime to be present in a good quality Portland cement clinker. He considered that the hydraulic constituent of clinker is tricalcium silicate with the structural formula



He pointed out that this material will be hydraulic because it is an anhydride and is thus capable of taking up water. He also considered that dicalcium silicate exists in two forms depending upon the temperature, thus

Thus on slow cooling the metasilicate will change to orthosilicate and, since the crystalline form in which the latter separates when first formed is unstable at ordinary temperatures, it dusts on cooling. The orthosilicate is non-hydraulic due to the absence of an anhydride grouping. However, if the metasilicate is cooled rapidly by quenching in water it remains as the metasilicate and is mainly vitreous and amorphous; hence the quenching hydrates it but slightly. By grinding finely, the hydraulic properties due to the anhydride grouping become more and more active. Meyer considered that in a Portland cement clinker completely saturated with lime the main constituents would be tricalcium silicate and tricalcium aluminate. Ordinary Portland cement clinker, however, consists of tricalcium silicate and double silicates of calcium, aluminium, and iron of the

type $5CaO.R_2O_3.SiO_2$. The aluminium, iron, and calcium are firmly united with silica, and hence there are present no simple calcium aluminates or ferrites.

Ludwig[16] considered that Alite is tricalcium silicate with the structural formula given to it by Meyer. He also supported Meyer's formula

$$x(3CaO.SiO_2) + y(5CaO.R_2O_3.SiO_2)$$

for Portland cement.

SYNTHETICAL RESEARCHES OF S. B. AND W. B. NEWBERRY (1897)[17].—These investigators burned at a white heat without fusion various well-ground homogeneous mixtures of pure materials. The products were tested for soundness by steaming a pat of neat set cement for five hours. (1) $2CaO.SiO_2$ dusted completely when cooled slowly, but there was no dusting when it was quenched in water. This portion gave a slow-setting sound product of satisfactory hardness in one and seven days. (2) $2.5CaO.SiO_2$ did not dust, gave a sound pat, but set slowly and hardened very slowly. (3) $3CaO.SiO_2$ did not dust, gave a sound pat, set slowly, but did not harden for several weeks. (4) $3.5CaO.SiO_2$ gave an unsound product. The observations on dicalcium silicate are in agreement with Meyer. The Newberrys concluded that the slow setting and hardening qualities of the more basic mixtures rendered them somewhat inferior. The $2CaO + SiO_2$ product alone was satisfactory from the point of reasonably rapid hardening, but its presence made dusting probable. The burn $2CaO + Al_2O_3$ gave a large rise in temperature when gauged, set in a few seconds, and was sound. Burns of CaO and Al_2O_3 containing more lime than 2CaO to one of alumina (in chemical equivalents) were unsound.

The Newberrys agreed with Le Chatelier and Meyer that tricalcium silicate was the most basic silicate that could exist in good cements, but they did not consider that a more basic aluminate than $2CaO.Al_2O_3$ was present. They further proved their contention by showing that cements prepared by them on the Le Chatelier formula $x(3CaO.SiO_2) + y(3CaO.Al_2O_3)$ were all unsound by the steam test, and increasingly so as the alumina content and consequently the excess CaO were raised. The burn $2CaO + Fe_2O_3$ gave a product inactive in cold water but which hardened rapidly in steam and was sound. The burn $3CaO.SiO_2 + 2CaO.Fe_2O_3$, containing 7 per cent. Fe_2O_3, was slow setting, sound, and hard. The burn $3CaO.Fe_2O_3$ was unsound, and the most basic ferrite is therefore $2CaO.Fe_2O_3$.

JEX[18] supported the Newberrys in the belief that dicalcium silicate was the main hydraulic agent in Portland cement.

Several workers failed to find any evidence for the existence of tricalcium silicate in Portland cement clinker.

WORMSER[19] studied the action of ammonium oxalate at red heat on Portland cement. From his results he said that the average composition of Portland cement was monocalcium silicate, $CaO:SiO_2$, 14 per cent.; dicalcium silicate, $2CaO.SiO_2$, 43 per cent.; dicalcium aluminate, $2CaO.Al_2O_3$, 23 per cent.; free calcium oxide, CaO, 20 per cent.

UNGER[20] fused several hundred pounds of dry cement slurry in an electric furnace and allowed it to cool slowly. Examination of the product led him to

the conclusion that Portland cement clinker is a mixture of several more or less well-defined chemical compounds and that tricalcium silicate does not exist in the clinker.

SCHOTT AND MICHAELIS[21] failed to obtain tricalcium silicate and concluded that it did not exist. They believed that Portland cement clinker was a mixture of calcium silicates and aluminates with varying amounts of uncombined calcium oxide ; when the molecular ratio $CaO.SiO_2$ exceeded 2.5, unsoundness resulted.

KEISERMAN[22] concluded from microscopic examination of synthetic burns that clinker consisted essentially of $4(2CaO.SiO_2) + 3CaO.Al_2O_3$.

(To be continued.)

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Synthesis of Calcium Silicates.

By S. NAGAI and K. MURAKAMI.

FURTHER results of the studies of the synthesis of calcium hydro-aluminates and calcium silicates carried out by Professors Nagai and K. Murakami at the Tokyo Imperial University are now available. The first stages of the work were described in this Journal for June, 1932, and the following gives the results of further investigations on the thermal synthesis of calcium silicates in which the results of the thermal synthesis of dicalcium silicate and tricalcium silicate under 1,400 deg. C. are reported.

Pure calcium carbonate and silicic acid anhydride were ground to fine powders and mixed in molecular relations of four kinds (*a*) $2CaCO_3 : SiO_2$ or $2CaO : SiO_2$, (*b*) $2.3CaCO_3 : SiO_2$ or $2.3CaO : SiO_2$, (*c*) $2.7CaCO_3 : SiO_2$ or $2.7CaO : SiO_2$, and (*d*) $3CaCO_3 : SiO_2$ or $3CaO : SiO_2$. These mixtures were heated at 1,300, 1,350 and 1,400 deg. C., from half an hour to twelve hours and some of them were treated by repeated heatings and grindings. The heating method and apparatus were the same as those used in the previous report. The heated products were tested for free lime, combined lime, insoluble or uncombined silica, and combined or soluble silica. By the calculation of the molecular ratio of combined lime to combined silica, the types of calcium silicates produced in each heated sample can be determined.

The results of synthesis of calcium silicates from the four mixtures show that lime and silica combined completely to dicalcium silicate by heating at 1,300 deg. C. for three hours in the case of the mixture (*a*) $2CaCO_3 : SiO_2$ (2 : 1). Synthesis of the mixture (*b*) $2.3CaCO_3 : SiO_2$ (2.3 : 1) shows that the reaction between $2CaO.SiO_2$ and CaO is very slow or difficult in the mixture of relatively low lime content $2.3CaO : SiO_2$ and for the low temperature heating. To promote the reaction the authors tried repeated grinding, mixing and heating the mixture (*b*) $2.3CaCO_3 : SiO_2$ (2.3 : 1). This was effective, and $3CaO.SiO_2$ was produced by three repetitions of heating at 1,400 deg. C. for nine hours. Synthesis of calcium silicates from the mixture (*d*) $3CaCO_3 : SiO_2$ (3 : 1) showed that continuous heating for longer than three hours was less effective. The repetition of heating, grinding and mixing was very effective and the more the lime content in the original mixture the larger the molecular ratio of combined line to combined silica. Two samples were obtained without dusting and appeared to be slightly sintered. It is interesting to note that $3CaO.SiO_2$ can be obtained in a nearly pure state by repeated heating, grinding and mixing.

A comparison of these results of synthesis by calculating the relative contents of $3CaO.SiO_2$ and $2CaO.SiO_2$ from the molecular ratios of combined lime to combined silica in every heated sample showed that $3CaO.SiO_2$ was produced in small amounts and it was easily produced in pure state even at such a low temperature as 1,400 deg. C. by the repeated heating, grinding and mixing.

To express more clearly the relations between continuous and repeated heating and the molecular ratios of combined lime to combined silica in the

heated samples, the graphical method is adopted by taking the molecular ratio as ordinate and heating hours or numbers of repetition of heating as abscissa, as shown in Figs. 1 and 2.

Studies on thermal synthesis of calcium silicates over 1,400 deg. C. and on some properties of the products were then undertaken. Pure calcium carbonate and silicic acid anhydride were ground to fine powder and mixed intimately in the molecular relations: (*a*) 2 : 1 in $2CaCO_3 : SiO_2$, (*b*) 2.3 : 1 in $2.3CaCO_3 : SiO_2$, (*c*) 2.7 : 1 in $2.7CaCO_3 : SiO_2$, (*d*) 3 : 1 in $3CaCO_3 : SiO_2$ and (*e*) 4 : 1 in $4CaCO_3 : SiO_2$. These mixtures were heated at 1,450 deg. C. and 1,500 deg. C. for several hours, and some of them were heated at these temperatures two, three or four times. The heating method and apparatus, and the testing method of the heated products were similar to those described. The results of the tests on the first four mixtures show that a temperature rise of only 50 deg. C. over 1,400 deg. C. is very effective and that by heating for three hours at 1,450 deg. C.

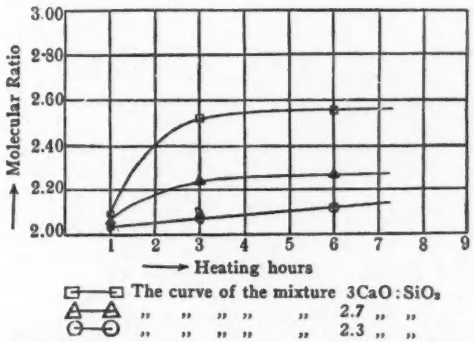

Fig. 1.—Molecular ratios and period of heating at 1,400 deg. C.

the reaction is almost completed. The effect of repeated heating and the law of mass action are clearly seen in these results. The results of synthesis of the last mixture ($4CaO : SiO_2$) prove that the free lime in these heated samples is estimated perfectly by the determination of free lime method adopted by the authors.

To ascertain what calcium silicates were produced in these samples, the authors calculated the components of the heated products and found that pure tricalcium silicate can be easily produced by heating at 1,450 deg. C. from the very fine raw mixture.

Using this sample of pure tricalcium silicate the problem of lime separation or setting free lime by reheating was studied, and it was found that tricalcium silicate dissociates in a small amount but not dicalcium silicate, and dicalcium silicate in $2.3CaO.SiO_2$ or $2.7CaO.SiO_2$ does not affect the decomposition of tricalcium silicate. It is clear that free lime in $4CaO : SiO_2$ accelerates the dissociation of lime from tricalcium silicate.

To ascertain why some salts accelerate this decomposition of lime from tricalcium silicate, several tests were made by adding a quantity of salt to the pure samples of tricalcium silicate. It is evident from the results that gypsum accelerates the decomposition of tricalcium silicate. In the presence of calcium fluoride, tricalcium silicate dissociates perfectly, but in this case the action of calcium fluoride does not seem to be perfectly catalytic. It is clear that calcium phosphate, magnesia and dicalcium silicate do not affect the dissociation of tricalcium silicate.

Studies were made on the hydraulic and physical properties of calcium silicates synthesised in the foregoing reports.

Pure calcium carbonate and silicic acid anhydride were mixed in the molecular relations (*a*) 2 : 1 in $2CaCO_3 : SiO_2$ or $2CaO : SiO_2$, (*b*) 2.3 : 1 in $2.3CaCO_3 : SiO_2$ or $2.3CaO : SiO_2$, (*c*) 2.7 : 1 in $2.7CaCO_3 : SiO_2$ or $2.7CaO : SiO_2$, and (*d*) 3 : 1 in $3CaCO_3 : SiO_3$ or $3CaO : SiO_2$. The mixtures were heated at 1,450 deg. C. once or twice for several hours in a gas furnace. The heated products were tested for free lime, free silica, combined lime, combined silica, etc.

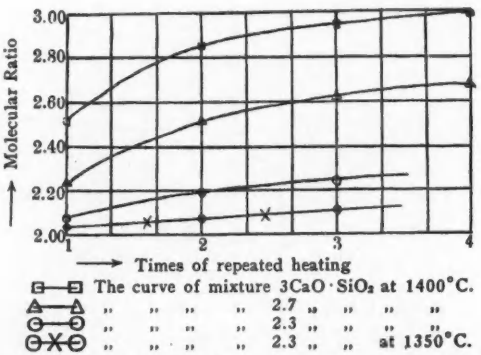

Fig. 2.—Molecular ratios and numbers of repetition of heating.

From the results, it is clear that mixture (*d*) is almost pure tricalcium silicate $3CaO.SiO_2$ and mixture (*a*) is almost pure dicalcium silicate $2CaO.SiO_2$, and mixtures (*b*) and (*c*) are the mixtures of these two silicates.

These four samples were used to study the hydraulic properties of calcium silicates. The small-piece testing method was used. The test pieces were cured in moist air for one day and immersed in water. $2CaO.SiO_2$ had not sufficient hydraulic property, and the test pieces cured even for three or seven days in moist air disintegrated as soon as they were immersed in water. From the results it is seen that pure tricalcium silicate, which was made at 1,450 deg. C., has very poor hydraulic properties.

Samples of $3CaO.SiO_2$, $2.7CaO.SiO_2$ and $2.3CaO.SiO_2$ were used to study the soundness of calcium silicates, using Le Chatelier's callipers. All the samples were satisfactory after five hours' boiling.

Samples of $3CaO.SiO_2$, $2CaO.SiO_2$ were used for the microscopical test of calcium silicates, together with samples made synthetically containing γ-$2CaO.SiO_2$ and β-$2CaO.SiO_2$; the latter was pure tricalcium silicate $3CaO.SiO_2$. Results of the microscopical tests showed that $3CaO.SiO_2$ and β-$2CaO.SiO_2$ were analogous and were pure tricalcium silicate $3CaO.SiO_2$, although the crystals in the latter were somewhat obscure while those in the former were purely cryptocrystalline. γ-$2CaO.SiO_2$ was seen to be the mixture of β- and γ-forms of dicalcium silicates.

By X-ray studies on samples of $2CaO.SiO_2$, γ-$2CaO.SiO_2$, $3CaO.SiO_2$ and β-$2CaO.SiO_2$ it was determined that the diffraction patterns of tricalcium silicate in the last two samples were the same and clearly different from those of the first two samples or of the mixture of β: and γ-$2CaO.SiO_2$.

Patent Applications.

398,028.—A. A. Thornton (Soc. Anon. Italiana per la Produzione Calci e Cementi di Segni).—Manufacture of hydraulic cements or binders.

Miscellaneous Advertisements.

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Influence of Temperature on the Strength of Concrete.

IN a publication of the Building Research Station (" Influence of Temperature upon the Strength Development of Concrete." N. Davey. Price 2s.), a description is given of recent investigations concerning the effect of temperature during the hardening of concrete. The following is an abstract of that portion of the experimental work which deals with temperature rise in mass concrete.

The rise in temperature of concrete during the process of setting and hardening may be very considerable. The amount of heat evolved, for example, in the case of rapid-hardening Portland cement may amount to as much as 80 calories per gram of cement after a period of three days, and in the case of high-alumina cement to 75 calories per gram after 24 hours. The rise in temperature per pound of cement per cubic yard of finished concrete may therefore approximate to 0.08 deg. C. (0.145 deg. F.) in the case of rapid-hardening Portland cement after 3 days, and to 0.075 deg. C. (0.135 deg. F.) in the case of high-alumina cement after 24 hours. In a large mass of Portland cement concrete (for example, 1 : 2 : 4 proportioned by weight) in which the cement content amounts to approximately 575 lb. per cubic yard of finished concrete, the temperature rise at the centre may approach 46 deg. C. (83.5 deg. F.) and the temperature gradient from the centre of the mass to the exterior surface may be as much as 15 to 20 deg. C. (27 to 36 deg. F.). The larger the mass and the higher the cement content the greater will be the rise in temperature.

The temperature at which concrete is cured has a marked effect upon the strength developed, hence at any given time, since a temperature gradient may exist throughout the mass, there will be a corresponding gradient of strength. Since other properties must also be affected the distribution and intensity of the stresses throughout the mass must vary considerably. It is only within the last few years that it has been realised that the expansion due to the heat of hydration of the cement followed by contraction on subsequent cooling has been largely responsible for cracks that have been observed in large concrete masses. For mass concrete work it is generally desirable to select a cement which has a slow evolution of heat, and in this connection the specification for the Hoover Dam in the United States calls for a cement in which the cumulative heat of hydration shall not exceed 60 calories per gram of cement after 7 days and 70 calories per gram after 28 days. A somewhat similar specification issued for the Pine Canyon Dam at Pasadena, California, calls for a cement in which the cumulative heat of hydration shall not exceed 65 calories per gram of cement at the age of 7 days and 80 calories per gram at 28 days, and that the tricalcium aluminate in the cement must not exceed 6 per cent. by weight.

The method used by some investigators for estimating the amount of heat evolved by hydrating cement consists in measuring the heat of solution of the hydrated cement at various times after mixing. A more direct method has been

in use for some time at the Building Research Station by which the maximum rise in temperature likely to occur in a large structure can be determined and the strength development can be followed.

Tests have been carried out on concrete prepared with normal and rapid-hardening Portland cements and with high-alumina cement. The concrete was proportioned by weight, using one part of cement, two parts of Ham river sand and four parts of Ham river gravel. The proportion of water was 60 per cent. by weight of the cement, and the mixing was carried out by machine for a period of two minutes.

For each series of tests 24 cylindrical test pieces measuring 6in. by 3in. were cast. One half of these were cured at 17 deg. C. (62.5 deg. F.) and the remainder adiabatically. In all cases the test pieces were formed in metal containers fitted with slip-on lids and rendered water-tight by placing a rubber band over the joint. There was therefore no transfer of moisture either to or from the test pieces. In all cases the strength development is more rapid when the concrete is cured under conditions similar to those at the centre of a large mass than when cured normally. The effect is not so marked in the case of normal Portland cement as in the case of rapid-hardening Portland cements. It would appear that the strength developed is a function of the heat evolved, and the greater the amount of heat generated in a given time the higher the strength provided that the heat is conserved.

Similar tests to those described were carried out on mixes using high-alumina cements. The tests show that there was a very pronounced falling off in strength after one day when the concrete was cured adiabatically, and that in the case of one cement, which was placed at a temperature of 35 deg. C. (95 deg. F.) the strengths attained were very much lower than those obtained at 17 deg. C. (63 deg. F.).

Two series of tests have been carried out to examine the influence of varying cement content upon the strength development of mass concrete. The first series comprised tests on rapid-hardening Portland cement, using mixes of the proportions 1 : 1 : 2, 1 : 2 : 4, and 1 : 3 : 6 by weight. The water contents were, 45, 60, and 75 per cent. of the weight of the cement for the mixes 1 : 1 : 2, 1 : 2 : 4 and 1 : 3 : 6 respectively. The test pieces were 6in. by 3in. cylinders and were tested at the ages of 1, 2 and 3 days, four cylinders being tested at each age. The temperature rise in the various mixes is shown in Fig. 1.

A similar series of tests was carried out using high-alumina cement. The grading of the sand and gravel was identical with that used for the tests on rapid-hardening Portland cement concrete. The proportions were 1 : $1\frac{3}{4}$: $3\frac{1}{2}$, 1 : 2 : 4, 1 : 3 : 6 and 1 : 4 : 8 by weight and the water contents were 58, 60, 95, and 125 per cent. by weight of the cement, respectively. The use of rich mixes of high-alumina cement is not recommended on account of the high temperature attained in the mass. Consequently it was considered unnecessary to experiment with mixes richer than 1 : $1\frac{3}{4}$: $3\frac{1}{2}$. Tests were made at 1, 2, and 3 days on cylindrical test pieces 6in. by 3in. in diameter and were compared with identical test pieces cured continuously at 17 deg. C. (63 deg. F.). The results show that the

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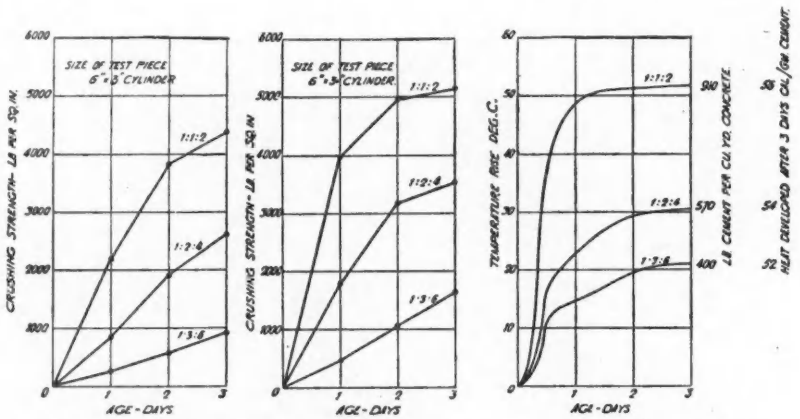
strength of high-alumina cement concrete at the interior of a large mass is likely to be considerably lower than that of a smaller concrete member from which the heat evolved has been rapidly dissipated. The rise in temperature in concrete prepared with rapid-hardening Portland cement and high-alumina cement after 3 days was plotted against the cement content in pounds per cubic yard of finished concrete, and showed in both cases the one to be directly proportional to the other.

A series of tests to examine the influence of the temperature of placement on the strength development of concrete was carried out, using rapid-hardening Portland cement. The grading of the sand and gravel was identical to that



A.—Crushing strength of rapid-hardening Portland cement concrete cured naturally.

B.—Crushing strength of rapid-hardening Portland cement concrete cured adiabatically.

C.—Temperature rise in rapid-hardening Portland cement concrete cured adiabatically.

Fig. 1.

used in the previous tests, the proportions of mix were 1 : 2 : 4 by weight, and the water content 60 per cent. by weight of the cement. The tests were carried out adiabatically on 6in. by 3in. cylinders which were broken at the ages of 1, 2, and 3 days. The mixes were placed at temperatures of 36.8 deg. F., 40.5 deg. F., 46.5 deg. F., 58 deg. F. and 65 deg. F.

The results illustrate that at whatever temperature the concrete has been placed the strength developed at any time is a function of the heat developed by the cement. For example, a mix placed at 58 deg. F. was found to have the same strength after 24 hours as an identical mix placed at 46.5 deg. F. after 2 days or as a mix placed at 36.8 deg. F. after 3 days, but in each case the amount of heat evolved was approximately the same.

The tests carried out adiabatically suggested that in a large block of concrete prepared with rapid-hardening Portland cement the strength after 3 days at the

centre of the block might be up to 30 per cent. greater than that of concrete nearer the outer face of the block. To obtain direct evidence on this point a block of rapid-hardening Portland cement concrete measuring 4ft. by 3ft. by 2ft. 6in. was cast. It was so arranged that a layer of forty-eight 6in. cubes could be cast at the mid-section of the mass and extracted after a period of 3 days. Rapid-hardening Portland cement was used. The mass was enclosed on three sides with 1in. wood shuttering and 6in. thickness of slag wool held in position with plywood sheets. The concrete block was bedded on 3in. of cork and was covered by a similar thickness of cork. The front of the mould was of timber 1in. thick and was left in position for 3 days.

Some difficulty was experienced in removing the specimens from the mass owing to slight disturbance of the cube formwork during casting, and the results were not so consistent as they would have been had this not occurred. However, the trend of the strengths is marked. Cubes taken from the mass after 3 days showed that the strength varied from approximately 3,500 lb. per square inch for concrete at the centre of the block to approximately 2,500 lb. per square inch for concrete near the exterior surface of the mass. The crushing strength of the cubes was found to be significantly correlated with the corresponding observed temperature.

A block of high-alumina cement concrete similar in composition to that used for the tests already referred to and measuring 4ft. by 3ft. by 2ft. 6in. was cast, and it was arranged that a layer of forty-eight 6in. cubes could be cast at the mid-section of the mass and extracted after a period of 3 days. The mass was enclosed on three sides with 1in. wood shuttering and 6in. thickness of slag wool held in position with plywood sheets. The concrete block was bedded on 3in. of cork and was covered by a similar thickness of cork. The front of the mould, which was of timber 1in. thick, was removed after 9 hours. No other attempt was made to keep the mass cool.

The strength of the cubes taken from the mass after three days showed that the strength varied from about 6,000 lb. per square inch for concrete near the exterior surface of the mass to about 2,500 lb. per square inch for that at the centre. A continuous temperature record was made at 11 points distributed in one-half of the mass at mid-section.

The temperature and strength at the centre of the mass very nearly approach the values determined on a small sample of the concrete in the adiabatically controlled chamber. At no point in the mass did the strength at three days reach the value obtained on concrete cubes cured under normal conditions at 15 deg. C.

Chemistry of Portland Cement.

With reference to the article in CEMENT AND CEMENT MANUFACTURE (June, 1933, page 203), Messrs. A. Guttmann and F. Gille point out that they have been successful in separating Alite and Celite from commercial cement clinker. The separation was made by a process of centrifuging, and the analysis of the Alite gave a composition equivalent to 93 per cent. tri-calcium silicate, while the composition of the Celite indicated a preponderance of the ternary compound $4CaO.Al_2O_3.Fe_2O_3$. These results were published in the years 1929 to 1931.

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Measurement of the Heat of Hydration of Cement.

TESTS on the development of heat of hydration of a standard Portland cement and a rapid-hardening Portland cement, are described in *Zement* (43/1933) by Ing. Dr. techn. R. Sandri, where reference is made to temperature measurements in dams and similar structures. It is pointed out that the amount of heat evolved can only be ascertained by systematic tests in a laboratory.

Earlier experiments by Woods, Steinour and Starke have been made by the indirect method of dissolving hydrated and unhydrated cement in acid and ascertaining the differences in the solution temperatures, which indicate the heat evolved. This method, while allowing comparison of different cements, is not sufficiently exact to supply information about the time factor.

Direct measurement is generally preferable and also allows the preparation of curves showing the heat evolved in relation to time. Adiabatic or isothermal methods may be used for this purpose, the disadvantage of the former being the speeding up of the reaction with consequent higher temperatures; the times of reaction as well as the temperatures obtained would never be reached in practice. The isothermal method—the temperature of the tested cement being kept con-

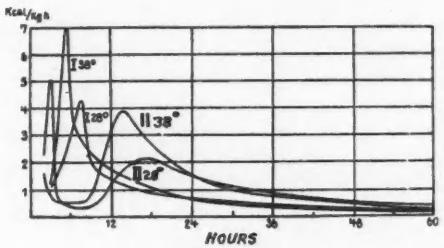

Fig. 1.

stant or nearly so—allows more satisfactory tests by measurement of the heat released.

The apparatus used is described and the results obtained are given for two series of tests at 28 deg. C. and 38 deg. C. In each case an ordinary Portland cement and a rapid-hardening Portland cement were examined. Fig. 1 shows the rate at which heat was evolved for the first 60 hours, kgcal. per hour and kg. of dry cement being given in relation to time. The areas below the curves represent the total heat of hydration; I indicates Portland cement, II indicates rapid-hardening Portland cement.

It will be seen that the temperature at which the test is carried out is of importance. Marked peaks are shown in each case, rapid-hardening Portland cement showing two. This occurrence cannot as yet be explained, but it seems to point to two separate reactions being in progress. The maximum of 28 deg.

for Portland cement and the first maximum of 28 deg. for rapid-hardening Portland cement coincide with the end of the setting time of the particular cement. The total heat evolved is constant and hardly influenced by the temperature of the test. This is illustrated by the crossing of the curves for the same cement. The larger quantity of heat released in the early stages as a result of the higher temperature is balanced by the smaller quantities later on.

The author is arranging further experiments and investigations on the influence of aggregate and the relations between the heat of hydration and tensile and compression strengths.

Book Review.

Manual del Cemento Portland. (Pp. 635. Published by Compania General de Asfaltos y Portland "Asland" de Barcelona.)—This book, in the Spanish language, deals principally with the practical uses of cement and is profusely illustrated with examples of concrete bridges, silos, chimneys, railway sleepers, etc., proper attention also being paid to the artistic applications of concrete. The manufacture of cement is not described, but there is a chapter on the geology and distribution of cement raw materials in Spain and Kuhl's work on the chemistry of cement is reproduced. The rest of the book is concerned with the design of concrete mixtures, calculations for reinforced concrete, specifications for cement and concrete, methods of testing, etc.

Change of Address.

Messrs. Mining & Industrial Equipment, Ltd., have removed their offices from 11, Southampton Row, W.C.1, to Aldwych House, Aldwych, London, W.C.2 (telephone, Holborn 2002).

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